



PII: S0025-326X(00)00082-5

Offshore Transport of Pesticides in the South Atlantic Bight: Preliminary **Estimate of Export Budgets**

HENRY A. ALEGRIA†*, J. PIERRE D'AUTEL‡ and TIMOTHY J. SHAW§

†Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA Department of Geography, University of South Carolina, Columbia, SC 29208, USA §Department of Chemistry and Biochemistry and Marine Science Program, University of South Carolina, Columbia, SC 29208, USA

Surface waters of the inner shelf (coast to 20-m isobath) of the South Atlantic Bight (SAB) were sampled in July 1994 and August 1995 for pesticides currently used in the south-eastern United States to estimate offshore transport. Only atrazine was detected at all stations in 1994 and 1995 and simazine was detected at all stations in 1995. Atrazine levels were 5.60-12 ng/l in July 1994 and 3.1-11 ng/l in August 1995 and simazine levels were 0.8-4.6 ng/l in August 1995. We calculated reservoir masses (in inner shelf waters) of 550 kg atrazine in July 1994, and 325 kg atrazine and 180 kg simazine in August 1995. Using these reservoir masses and a previously estimated residence time for waters of the inner shelf of 30 days, annual export budgets were calculated. For 1994, a budget of 6600 kg atrazine was calculated. For 1995, budgets of 3900 kg atrazine and 2150 kg simazine were calculated.

Yearly riverine discharge to estuaries in the study region was estimated to range from 600 to 5600 kg atrazine and 100 to 550 kg simazine. The large budgets for the coastal inner shelf compared with yearly riverine discharge suggest that a significant fraction of atrazine and simazine applied in the region is being transported offshore from coastal waters. This transport pathway needs to be factored in when calculating mass balances and determining the ultimate fate of these pesticides. © 2000 Published by Elsevier Science Ltd.

Keywords: triazines; South Atlantic Bight; offshore transport.

Introduction

The widespread appearance of pesticides in the environment (soil, water and air) has led to increased interest in understanding their cycling in the environment.

*Corresponding author.

E-mail address: shaw@psc.sc.edu (T.J. Shaw).

It has been recognized that once pesticides are applied, they may be transported over considerable distances through soil, groundwater, surface runoff and in air (e.g., Alegria and Shaw, 1999; Cogger et al., 1998; Wania and Mackay, 1996; Pereira and Hostettler, 1993; Burkhart and Kolpin, 1993). In order to determine the environmental impact of pesticides, it is necessary to determine the extent to which they are transported in each of these media. Studies have shown that the extent of movement in each of these media depends on many variables, including physico-chemical properties of the herbicides and soil, methods of application, and ambient conditions during and after application (e.g., prevailing temperatures and the extent and timing of rainfall).

One transport pathway for pesticides that has not been well studied is the offshore transport from estuarine waters to surface waters of the coastal ocean. It is becoming increasingly clear, however, that this is one area that must be addressed if a more complete understanding of transport mechanisms of pesticides is to be attained. Zhou et al. (1996) state that the quantitative fluxes and fates of hydrophobic organic micropollutants 'along the environmental continuum from catchment to rivers, and to estuary and coastal seas have rarely been rigorously mass-balanced' (added emphasis). Sunderman and Radach (1997) point out that the knowledge regarding regional fluxes, turnover rates and budgets of contaminants in coastal waters is still at an early stage. This is especially true with regard to currently used pesticides such as triazines. These were designed to break down quickly, but due to their fairly high solubilities their potential impact on the coastal ocean via surface runoff is significant (Chernyak et al., 1996).

Many national and international projects are therefore addressing budgets and fluxes of contaminants, including pesticides, in coastal waters. In the North Sea, for example, a multinational effort has been underway for some years to document levels and movement of contaminants (Sundermann and Radach, 1997). Recently, a series of reports documented annual budgets

and fluxes of lead, suspended particulate matter, hexachlorocyclohexanes, polychlorinated biphenyls and triazines in the German Bight, a subsection of the North Sea (Sunderman and Radach, 1997; Puls et al., 1997a,b; Huhnerfuss et al., 1997). Bester and Huhnerfuss (1993) measured levels of triazines in the German Bight in January 1991 and the Baltic Sea in May 1991. Gough et al. (1994) carried out a survey to determine the levels of Irgarol 1051 (an s-triazine antifouling compound) and triazines in the coastal waters of southern England during July-September 1993. Zhou et al. (1996) determined the distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber estuary and Humber coastal zone in England during January/February and June 1995. Readman et al. (1993) reported that atrazine and simazine were below their detection limits in coastal waters of Cote d'Azur, France. These studies suggest that in areas of large-scale agriculture, the coastal ocean could be significantly impacted by pesticides and point to the need for further studies regarding the offshore movement of pesticides to coastal waters.

During July 1994 and August 1995, we carried out a survey of coastal waters of the south-eastern US (Figs. 1 and 2) to measure levels of pesticides currently used in this region. The goal of this project was to determine the budget of these pesticides in the inner shelf (the subsection of coastal ocean extending from the coast to the 20-m isobath, which is described in more detail below) and make preliminary estimates of the extent of offshore transport of pesticides from local sources. Large-scale agriculture in the south-eastern US has resulted in the heavy usage of many pesticides in this region (Gianessi and Anderson, 1995; Pait et al., 1992). This region also has several major rivers which drain agricultural lands and empty into the Atlantic Ocean. Consequently, the coastal ocean in this region may be impacted by pesticides, especially soluble ones. This region thus represents an ideal study site to determine the importance of offshore transport of currently used pesticides from estuaries to the coastal ocean.

Experimental

Study area

The South Atlantic Bight (SAB) refers to waters off the south-eastern coast of the United States, extending from approximately Cape Hatteras, North Carolina to West Palm Beach, Florida (Kourafalou et al., 1996a). Nine major rivers discharge freshwater into the continental shelf of the SAB (Blanton and Atkinson, 1983). Waters of the SAB can be divided into three regions: the inner shelf (which extends from the coast to the 20-m isobath), the midshelf (depths between 20 and 40 m) and the outer shelf (extending from the 40-m isobath to the shelf break) (Kourafalou et al., 1996a; Wong, 1995; Blanton and Atkinson, 1983). In the inner shelf, tidal mixing blends the discharges from the rivers into a band of freshened water (referred to as the 'coastal boundary zone' by Blanton and Atkinson, 1983), which extends 20-30 km offshore. Previous studies have shown that the inner shelf behaves as a discrete environment, distinct from estuaries or the open ocean (Shaw et al., 1998; Moore, 1996; Kourafalou et al., 1996a; Wong, 1995; Blanton and Atkinson, 1983). The inner shelf (particularly off South Carolina and Georgia) stores riverborne

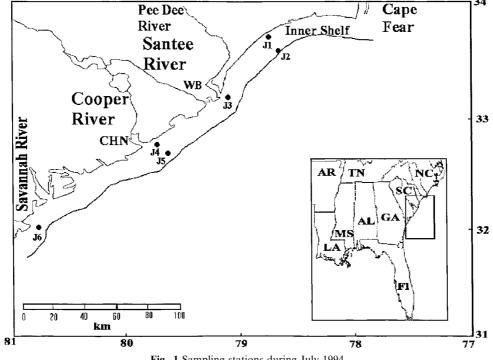


Fig. 1 Sampling stations during July 1994.

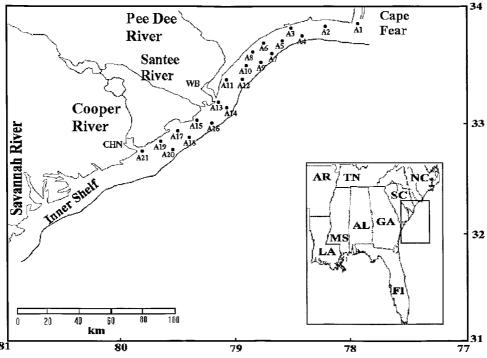


Fig. 2 Sampling stations during August 1995.

materials and exchanges them with the midshelf and outer shelf. Blanton and Atkinson (1983) and Kourafalou *et al.* (1996a,b) showed that circulation of inner shelf waters is northward during spring and summer and southward during autumn. This leads to exchange of inner shelf waters with mid-shelf waters off the South Carolina coast in spring and off Florida in autumn (Blanton and Atkinson, 1983; Kourafalou *et al.*, 1996a,b).

Sampling

Samples were collected during two cruises to the SAB during 6–17 July 1994 and 11–21 August 1995 on the RV *Cape Hatteras*. In July 1994, six stations and in August 1995, 21 stations inside the inner shelf were sampled (Figs. 1 and 2).

Sampling was carried out by pumping water from the coastal ocean from approximately 2 m below the surface to avoid surface microlayer artefacts. In 1995, some stations were also sampled at depths from 6 to 15 m (time limitations did not permit sampling multiple depths at every station). In 1994, water was pumped using a peristaltic pump through 1.25-cm i.d., teflonlined tubing into 18-1 stainless steel canisters which had been rigorously cleaned before the cruise (Alegria and Shaw, 1999). In 1995, water has pumped using a submersible pump through high-density polyethylene tubing at a rate of about 80 l/min. Prior to the cruise, distilled water was circulated through this tubing for several hours daily over several weeks, and during the cruise seawater was circulated through it for several minutes before each sample was collected. This was to

minimize sampling artefacts. Samples ranged from 36 to 72 l. On board, water was pressure-filtered through 293 mm (1 μm nominal pore size) glass fibre filters (prebaked at 450°C overnight) and the filtered water was pulled through a glass column with XAD-2 resin at 200–250 ml/min using a peristaltic pump (Kucklick et al., 1996). Glass fibre filters (GFFs) were wrapped in prebaked and solvent-washed aluminium foil and stored in a freezer, and XAD-2 resin was stored in pre-cleaned glass jars in a refrigerator until analysis.

Extraction and analysis

Pesticides were extracted from GFFs and XAD-2 resin as in Alegria and Shaw (1999). Briefly, GFFs and XAD-2 were soxhlet-extracted for 24 h with 200 ml of a 1:1 mixture of acetone and hexane. After soxhlet extraction, the acetone-aqueous phase was removed by partitioning into 100 ml E-pure water into which NaCl was added. The acetone fraction was back-extracted into 75 ml hexane twice. The combined hexane extracts were concentrated to 1 ml and subjected to column chromatography using Florisil as detailed in Alegria and Shaw (1999). Triazines and organophosphate pesticides were measured by gas chromatography-electron impact mass spectrometry (GC/MS). 1994 samples were analysed using a Finnegan instrument (Alegria and Shaw, 1999), and 1995 samples were analysed using an HP 5890II instrument, both equipped with a 30 m \times 0.25 mm i.d. ×0.25 µm DB-5 (J&W Scientific) capillary column. Samples (2 µl) were injected at 90°C splitless. After a 1 min hold, the oven was programmed at 5°C/min to 300°C with a 10 min hold. Injector was set at 250°C and detector at 275°C. Sensitivity was enhanced by operating in the selected ion monitoring (SIM) mode. SIM ions used were detailed in Alegria and Shaw (1999).

After analysis by GC/MS, samples were diluted to 1 ml with iso-octane, mirex was adjusted to 10 µg/l in the dilution and trifluralin, linuron, alachlor and metolachlor were measured by gas chromatography-electron capture detection (GC/ECD). 1994 samples were analysed using a Varian 3700 gas chromatograph (Alegria and Shaw, 1999) and 1995 samples were analysed using an HP 5890II Plus instrument, both equipped with a 30 m×0.25 mm i.d.×0.25 μm DB-5 (J&W Scientific) capillary column. Both sets of samples were injected at 90°C spiltless (30 s split time). After a 1 min hold, the temperature was programmed at 5°C/min to 300°C with a 10 min hold. Carrier gas was He at 60 cm/s with N₂ as a detector make-up gas at 50 ml/min. Injector temperature was 250°C and detector temperature was 275°C. Pesticides were quantified relative to the internal standard mirex from a calibration plot of 4-5 standards which bracketed the concentrations of pesticides in samples.

Results and Discussion

Quality control

For both sets of samples, three solvent blanks were measured by adding 500 ml of solvents to clean volumetric flasks and treating as samples. Limits of detection for atrazine and simazine, the two pesticides detected consistently, were 0.1 ng/l. Five spikes were measured by adding analytes in acetone to 1 or 2 l of deionized (Epure) water at concentrations of 100 ng/l – 10 µg/l and treating as samples. Average recoveries for pesticides that were consistently detected were: atrazine 80 \pm 10% and simazine 81 \pm 12%. Concentrations reported in this study were corrected for recoveries.

Pesticide concentrations

In July 1994, only atrazine and metolachlor were detected at all stations, and trifluralin (at significantly lower concentrations) at four of six stations. In August 1995, only atrazine and simazine were detected consistently at the sampling stations. It is possible that simazine was not detected in July 1994 because of the lack of adequate coverage of the sampling region (Fig. 1). Atrazine (200 000 kg), alachlor (165 000 kg), metolachlor (111 000 kg) and chlorpyrifos (85 000 kg) were the most heavily used pesticides in estuarine drainage areas within our study region (Gianessi and Anderson, 1995; Pait et al., 1992). In comparison, application of all other pesticides targeted in this study were used in considerably smaller quantities, ranging from approximately 8000 kg (azinphosmethyl) to 50 000 kg (carbaryl). This may explain the absence of some pesticides in coastal waters since most surface runoff may have occurred immediately after application (April and May) and any transportation to estuaries, and offshore, by the time of our sampling occurred at undetectable levels. In addition, some pesticides (e.g., trifluralin, chlorpyrifos, propazine) are virtually insoluble in water, and some (e.g., trifluralin, chlorpyrifos, methyl parathion, azin-phosmethyl, diazinon, linuron, carbaryl) are strongly adsorbed onto particulates (EXTOXNET). This combination of lower solubilities and stronger adsorption to particulates may explain the absence of many of the pesticides targeted in this study since these pesticides would be less susceptible to transportation by surface runoff. In addition, some pesticides may be degraded quickly, which may account for their absence. Alachlor, chlorpyrifos, azinphosmethyl, and methyl parathion, for example, have been shown to degrade fairly quickly, so they may have degraded completely by the time of our sampling (Goolsby *et al.*, 1997).

The presence of atrazine in coastal waters during both July and August may also reflect a significant atmospheric reservoir. Previous studies measuring pesticide levels in rainfall have reported that atrazine can be detected year-round (Goolsby et al., 1997; Struger and Chan, 1996; Glotfelty et al., 1990). Studies have indicated that the large quantities used in the US, combined with a long half-life in soils and a relatively low vapour pressure results in a slow, steady volatilization of atrazine over long periods of time. This results in a significant year-round atmospheric reservoir which leads to annualized deposition in coastal waters directly and indirectly (Alegria and Shaw, 1999). Such an atmospheric reservoir does not exist for other pesticides with low usage and/or low soil half-lives and higher vapour pressures, which lead to high volatilization immediately following application.

Table 1 shows the concentrations of atrazine and simazine measured in 1994 and 1995. In July 1994, atrazine concentrations in surface waters ranged from 5.6 to 12 ng/l (average of 8.6 ng/l). In August 1995, surface water concentrations for atrazine ranged from 3.1 to 11 ng/l (average of 5.1 ng/l) and for simazine from 1.5 to 4.8 ng/l (average of 2.8 ng/l). Both atrazine and simazine were below detection limits for most samples taken at depths of 10–15 m (Table 1). Samples taken at 6 m usually had atrazine and simazine concentrations similar to surface samples (Table 1), consistent with a well-mixed surface water column.

Table 2 compares the levels measured in this study with previously reported levels in other coastal areas. Atrazine levels during both sampling periods were generally similar to levels in the Baltic Sea in May 1991 (Bester and Huhnerfuss, 1993) and the English Channel during July–September 1993 (Gough *et al.*, 1994); somewhat higher than levels in the Humber Coastal Zone of England in January/February and June 1995 (Zhou *et al.*, 1996), the German Bight in 1997 (Huhnerfuss *et al.*, 1997); and considerably lower than levels in the German Bight in May 1991 (Bester and Huhnerfuss, 1993). Simazine levels in our study in August 1995 were generally similar to levels in the German Bight in 1997 (Huhnerfuss *et al.*, 1997) and lower than

TABLE 1
Concentrations of atrazine and simazine in the SAB (ng/l) in 1994 and 1995.^a

Station	Atrazine (July 1994)	Atrazine (August 1995)	Simazine (August 1995)
J1	5.4		
J2	6.0		
J3	6.0		
J4	6.5		
J5	12.3		
J6	12.6		
A1		6.1	3.5
A2		5.1	2.1
A3		4.9 (6 m - 4.8)	2.3 (6 m - 1.9)
A4		6.1 (6 m - 6.0)	1.5 (6 m - 1.3)
A5		6.0	1.6
A6		4.3 (10 m - BD)	2.1 (10 m - BD)
A7		4.3	3.4
A8		4.3	2.1
A9		5.2 (6 m - 4.8)	2.4 (6 m - 2.2)
A10		4.1	3.5
A11		6.1 (10 m - 0.2)	3.2 (10 m – BD)
A12		5.6 (6 m – 5.2)	4.8 (6 m – 4.3)
A13		5.2	4.0
A14		4.6	2.8
A15		4.5	2.3
A16		5.8 (10 m – BD)	3.2 (10 m – 0.1)
A17		6.6	3.1
A18		6.1 (6 m – 5.3)	2.8 (6 m – 2.5)
A19		5.7	3.5
A20		4.9 (10 m – 0.1)	3.4 (10 m – BD)
A21		4.3 2.0	

^a BD – below detection limits.

levels in the Baltic Sea and the German Bight in May 1991 (Bester and Huhnerfuss, 1993) and the English Channel in January/February and June 1995 (Zhou *et al.*, 1996).

Calculation of export budgets

As noted above, the inner shelf of the SAB can be considered a discrete environment, distinct from estuaries and the open ocean (Shaw et al., 1998; Moore, 1996; Kourafalou et al., 1996a,b; Wong, 1995; Blanton and Atkinson, 1983). Therefore, we can estimate the integrated budget of atrazine and simazine for this section of the SAB by multiplying the average pesticide concentrations by the volume of water in the inner shelf (assuming homogenous mixing). Moore (1996) showed through salinity and temperature profiles that the py-

cnocline of the inner shelf of the SAB extended to a depth of at least 10 m and calculated the volume of the inner shelf in our region of study to be 6.4×10^{10} m³ to this depth. Using this volume, our calculations resulted in total masses of approximately 550 kg atrazine for July 1994, and 325 kg atrazine and 180 kg simazine for August 1995. Moore (1996) determined the residence time of waters in the inner shelf to be 30 days. Using this residence time, our numbers would translate to a yearly integrated export budget of approximately 6600 kg atrazine in 1994, 3900 kg atrazine in 1995 and 2150 kg simazine in 1995 to mid-shelf waters. These are admittedly rough estimates but they provide a first estimate of the annual budget of atrazine and simazine in the inner shelf of the SAB.

Pesticides are applied locally, south-eastern US, between late April and May (Pait et al., 1992). Studies have shown that most surface runoff to estuaries occurs immediately after application (Kucklick and Bidleman, 1994). Therefore, transport from estuaries to the coastal ocean should be highest during late April and May and should gradually decrease as estuaries receive less input from agricultural lands. Consequently, although estimating yearly budgets using a single month's concentrations may result in overestimation compared with budgets using later months (post-August), it results in underestimation compared with budgets calculated using earlier (March-June) months. Calculating annual budgets using a single month is equivalent to integrating over a one-year period the quantities of pesticides transported offshore during a few months. There will be some uncertainty in the results, but the estimates provide a first approximation of annual export budgets of atrazine and triazine to midshelf waters in the region.

In a related study (Alegria and Shaw, 1999), we estimated the yearly riverine discharge of atrazine into estuaries in the region to be 600–5600 kg. Kucklick and Bidleman (1994) estimated a yearly discharge of 3100 kg (3.1 t) atrazine into Winyah Bay, whose watershed receives approximately 80% of the total atrazine applied in South Carolina (Pait *et al.*, 1992). We estimate the yearly discharge of simazine into the region's estuaries to be 550 kg using data from Kucklick and Bidleman (1994), and approximately 100–510 kg using the same

TABLE 2
Comparison of concentrations in the inner shelf of SAB with other regions.

Location	Atrazine (ng/l)	Simazine (ng/l)	
SAB (July 1994)	5.4–12.6 (mean: 8.6)	Not detected	
SAB (August 1995)	3.1–11.0 (mean: 5.1)	1.5–4.8 (mean: 2.8)	
Baltic Sea (May 1991)	2–11 (mean: 4)	3–13 (mean: 5)	
German Bight (May 1991)	1–110 (mean: 19)	4–200 (mean: 70)	
English Channel (July–September 1993)	5–12 (mean: 6)	5–12 (mean: 8)	
Cote d'Azur, France	Not detected	Not detected	
Humber Coastal Zone	< 10	Not reported	
(January/February, June 1995) German Bight (1997)	Mean: 3.3	(Mean: < 2)	
Octinali Digit (1997)	wicall. 5.5	(ivicali. < 2)	

TABLE 3

Input of atrazine and simazine into estuaries and inner shelf annual budgets in the SAB.

	Atrazine (kg)	Simazine (kg)	References
Quantity applied per year	195 068	25 563	Gianessi and Anderson (1995)
Quantity discharged into estuaries	600–5600	100–550	Alegria and Shaw (1999), This work
Estimated annual budgets in inner shelf waters	3900 (1994), 6600 (1995)	2150 (1995)	This work

calculations as in Alegria and Shaw (1999). Table 3 summarizes our calculations/estimates.

A comparison of the integrated annual budgets calculated for coastal waters of the inner shelf (6600 kg atrazine in 1994, and 3900 kg atrazine and 2150 kg simazine in 1995) with estimated annual riverine input into the region (600-5600 kg atrazine and 100-550 kg simazine) suggests that significant quantities of atrazine and simazine are transported offshore in the SAB, quantities in the order of those known to be discharged into estuaries. Triazines are fairly water soluble, which facilitates their movement in the dissolved phase through surface runoff into estuaries and out into the coastal ocean. These results are important in calculating mass balances of pesticides in the estuarine areas. Previous studies have not adequately addressed the fact that estuaries do not represent a final sink for pesticides from areas of application, but instead represent one region in the continuum from the application sites to the ocean. Our results indicate that the offshore transport of triazines may represent an important mechanism which must be included in determining their ultimate fate. This was not the case for other pesticides targeted in this study which are used in smaller quantities (e.g. azinphosmethyl, diazinon, methyl parathion, carbofuran), or whose properties result in less transport via surface runoff (e.g., trifluralin, chlorpyrifos, methyl parathion, azinphosmethyl, carbaryl, linuron).

These results may also indicate that the impact of triazines in estuarine areas might not be as significant as would be expected from the quantities discharged into those systems via riverine discharge. If a significant fraction of the triazines that are discharged into estuaries are then transported offshore, then ocean water may simply dilute them and minimize any negative environmental effects. Thus, it may be incorrect to determine the potential impact of triazines on the estuarine ecosystem based on quantities discharged by rivers without factoring in quantities leaving the system into the coastal ocean via offshore transport.

The magnitude of atmospheric deposition (wet and dry) of atrazine and simazine to the area is still unknown. Such information would enable us to estimate the importance of this mechanism as a contributor to the annual budget. In a related study (Alegria and Shaw, 1999), we estimated that a 2–3 day rain event related to Tropical Storm Alberto deposited 130–495 kg atrazine into the SAB. This is a significant quantity and suggests that atmospheric wet deposition may contribute signif-

icantly to the budget of the coastal waters of SAB. Dry deposition may also be significant, especially considering the large quantities of triazines used in the US and the likelihood of a significant year-round reservoir.

In addition, during the 1994 cruise there was high riverine discharge into the SAB because of intense rainfall that had occurred in the south-eastern US from Tropical Storm Alberto and related storm events (Moore et al., 1998; Hale, 1994; Hippe et al., 1994). The Savannah River's discharge, for example, peaked at approximately 700 m³/s on 11 July and was around or above 600 m³/s during the cruise (Moore et al., 1998). The Pee Dee River's discharge was also higher than normal during the July 1994 cruise due to the rainfall on land (Moore et al., 1998). These elevated discharges probably resulted in an increased input of atrazine, one of the most widely used pesticides in the south-eastern US, via surface runoff. During the August 1995 cruise river discharges were normal, and the 1995 budget is probably more reflective of riverine input.

As we note above, our budgets for waters of the inner shelf represent integrated budgets. As pointed above, tidal mixing and wind movement result in a blending of riverine discharges into a distinct volume of water. Our budgets thus represent riverine discharge, advective transport, atmospheric deposition and groundwater discharge into the coast. It has been suggested that there may be significant contribution from groundwater discharge, but this is unlikely considering the small volume of *freshwater* discharge via this pathway (W. Moore, pers. comm.).

Our results are generally similar to those of Huhnerfuss *et al.* (1997) for the German Bight. These authors calculated an input of approximately 4900 kg (4.9 t) atrazine and 27 100 kg (27.1 t) simazine via rivers; 9300 kg (9.3 t) atrazine and <5700 kg (5.7 t) simazine via inflow of waters at the western edge of the bight; and approximately 500 kg (0.5 t) triazines (atrazine + simazine + terbutylazine) via atmospheric deposition. At the northern edge of the bight, they estimated an annual outflow of 44 000–103 000 kg (44–103 t) atrazine and 5600–54 000 kg (5.6–54 t) simazine. They concluded that riverine input of triazines to the coastal ocean was important in the region.

Kourafalou *et al.* (1996a,b) simulated the path and fate of riverborne material in the SAB. They concluded that most surface material is transported northwards during spring and is eventually exchanged with the midshelf, and that within 60 days half of all material was

in the outer shelf and half had left the shelf region. During autumn, transport southward is favoured and surface particles are exchanged into the open ocean off the Florida coast. These processes should govern the transport of pesticides away from the inner shelf into the open ocean. Moore (in press) has shown via the use of Ra isotopes that the aging and mixing of the water from the inner shelf offshore is a clear transport function, as should be the case with pesticides.

Conclusion

We sampled waters of the inner shelf in the SAB during July 1994 and August 1995 for pesticides currently used in the south-eastern US. During July 1994, concentrations of atrazine averaged 8.6 ng/l and during August 1995 concentrations averaged 5.1 ng/l. Concentrations of simazine during August 1995 averaged 2.8 ng/l. We estimated the yearly export budget of atrazine to be 6600 kg in 1994 and 3900 kg in 1995, and the yearly export budget of simazine to be 2100 kg for 1995. A comparison of these annual budgets of atrazine and simazine with estimated yearly riverine discharges into estuaries in the area (600–5600 kg atrazine and 100–550 kg simazine) suggests that there is significant offshore transport into the coastal ocean of the atrazine and simazine applied in the region.

These results suggest that when using mass balances to account for the fate of atrazine and simazine, their offshore transport from estuaries must be included to obtain an accurate picture. These results also suggest that perhaps these pesticides may not have as significant an impact in estuaries as would be suggested solely by quantities discharged by rivers since a significant fraction would be transported offshore and eventually into the open ocean.

These results are preliminary, but they represent an important first approximation of the extent of offshore transport of herbicides in the SAB. Generating more refined budget estimates would require sampling several times during the year to account more accurately for temporal variations and calculating the contribution from atmospheric deposition to the total budget.

This research was supported by NSF grant OCE-9314587. We thank Dr Willard Moore for his help in setting up the sampling cruises. We also thank the captain and crew of the RV *Cape Hatteras*, Deedra Foxworth and Jeremiah Kloepfer for their help with sampling. We also thank Dr Terry Bidleman and two anonymous reviewers for their suggestions to greatly improve the manuscript. We also thank Dr William Cotham and Dr Mike Walla of the USC Mass Spectrometry facility for their help in carrying out the analysis.

- Alegria, H. A. and Shaw, T. J. (1999) Rain deposition of pesticides in coastal waters of the South Atlantic Bight. *Environmental Science* and Technology 33, 150–154.
- Bester, K. and Huhnerfuss, H. (1993) Triazines in the Baltic and North Sea. *Marine Pollution Bulletin* **26**, 423–427.
- Blanton, J. O. and Atkinson, L. P. (1983) Transport and fate of river discharge on the continental shelf of the south-eastern United States. *Journal of Geophysical Research* 88, 4730–4738.

- Burkhart, M. R. and Kolpin, D. W. (1993) Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. *Journal of Environmental Quality* 22, 646–656.
- Chernyak, S. M., Chernyak, M. and McConnell, L. L. (1996) Evidence of currently used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. *Marine Pollution Bulletin* 33, 410–419.
- Cogger, C. G., Bristow, P. R., Stark, J. D., Getzin, L. W. and Montgomery, M. (1998) Transport and persistence of pesticides in alluvial soils: I. Simazine. *Journal of Environmental Quality* 27, 543– 550
- EXTOXNET (Extension Toxicology Network); available on the Internet at http://ace.orst.edu/info/extoxnet.
- Gianessi, L. P. and Anderson, J. E. Pesticide Use in South Carolina Crop Production. National Center for Food and Agricultural Policy, Washington DC, 1995.
- Glotfelty, D. E., Williams, G. H., Freeman, H. P. and Leech, M. M. (1990) Regional atmospheric transport and deposition of pesticides in Maryland. In *Long Range Transport of Pesticides*, ed. D. A. Kurtz, pp. 1199–1223. Lewis Publishers, Chelsea, MI, USA.
- Goolsby, D. A., Thurman, E. M., Pomes, M. I., Mayer, M. and Battaglin, W. A. (1997) Herbicides and their metabolites in rainfall: origin, transport, and deposition patterns across the midwestern and north-eastern United States, 1990–1991. *Environmental Science and Technology* 31, 1323–1333.
- Gough, M. A., Fothergill, J. and Hendrie, J. D. (1994) A survey of southern England coastal waters for the s-triazine antifouling compound Irgarol 1051. *Marine Pollution Bulletin* 28, 613–620.
- Hale, H. T. (1994) The independence day flood of 1994. In USGS Yearbook, fiscal year 1994.
- Hippe, D. J., Wangsness, D. J., Frick, E. A. and Garrett, J. W. (1994) Water quality of the Apalachicola-Chattahoochee-Flint and Ocmulgee River Basins Relating to Flooding from Tropical Storm Alberto; Pesticides in Urban and Agricultural Watersheds; and Nitrate and Pesticides in Ground Water, Georgia, Alabama, and Florida. USGS Water-Resources Investigations Report 94-4183, 1994.
- Huhnerfuss, H., Bester, K., Landgraff, O., Pohlmann, T. and Selkes, K. (1997) Annual balances of hexachlorocyclohexanes, polychlorinated biphenyls and triazines in the German Bight. *Marine Pollution Bulletin* **34**, 419–426.
- Kourafalou, V. H., Lee, T. N., Oey, L.-Y. and Wang. J. D. (1996a) The fate of river discharge on the continental shelf 2. Transport of coastal low-salinity waters under realistic wind and tidal forcing. *Journal of Geophysical Research* 101, 3435–3455.
- Kourafalou, V. H., Oey, L.-Y., Wang, J. D. and Lee, T. N. (1996b) The fate of river discharge on the continental shelf 1. Modeling the river plume and the inner shelf coastal current. *Journal of Geophysical Research* 101, 3415–3434.
- Kucklick, J. R. and Bidleman, T. F. (1994) Organic contaminants in Winyah Bay, South Carolina I: Pesticides and polycyclic aromatic hydrocarbons in subsurface and microlayer waters. *Marine Envi*ronmental Research 37, 63–78.
- Kucklick, J. R., Harvey, H. R., Ostrom, P. H., Ostrom, N. E., Baker, J. E. (1996) Organochlorine dynamics in the Pelagic Food Web of Lake Baiker. *Environmental Toxicology and Chemistry* 15, 1388– 1400.
- Moore, W. S. (1996) Large groundwater input to coastal waters revealed by Ra-226 enrichments. *Nature* **380**, 612–614.
- Moore, W. S., Kjerfve, B. and Todd, J. F. (1998) Identification of rainfreshened plumes in the coastal ocean using Ra isotopes and Si. *Journal of Geophysical Research* **103**, 7709–7717.
- Moore, W. S. (in press) Determining coastal mixing rates using radium isotopes. *Continental Shelf Research*.
- Pait, A. S., DeSouza, A. E. and Farrow, D. R. G. (1992) Agricultural Pesticide Use in Coastal Areas: A National Summary. National Oceanic and Atmospheric Administration, Rockville, MD, USA.
- Pereira, W. E. and Hostettler, F. D. (1993) Nonpoint source contamination of the Mississippi River and its tributaries by herbicides. *Environmental Science and Technology* 27, 1542.
- Puls, W., Gerwinski, W., Haarich, M., Schirmacher, M. and Schmidt, D. (1997a) Lead budget for the German Bight. *Marine Pollution Bulletin* 34, 410–418.
- Puls, W., Heinrich, H. and Mayer, B. (1997b) Suspended particular matter budget for the German Bight. *Marine Pollution Bulletin* 34, 398–409.

- Readman, J. W., Wee Kwong, L. L., Grondin, D., Bartocci, J., Villeneuve, J.-P. and Mee, L. D. (1993) Coastal water contamination from a triazine herbicide used in antifouling paints. *Environ*mental Science and Technology 27, 1940–1942.
- Shaw, T. J., Moore, W. S., Sochaski, M. A. and Kloepfer, J. (1998)
 The flux of barium to coastal waters of the south-eastern USA: the importance of submarine groundwater discharge. *Geochimica et Cosmochimica Acta* 62, 3047–3054.
 Struger, J. and Chan, C. H. (1996) Occurrence and transport of
- Struger, J. and Chan, C. H. (1996) Occurrence and transport of herbicides in precipitation from the Canadian section of the Great Lakes Basin. Presented at the 17th Annual SETAC Meeting, Washington DC, 17–21 November.
- Sundermann, J. and Radach, G. (1997) Fluxes and budgets of contaminants in the German Bight. Marine Pollution Bulletin 34, 395–397
- Wania, F. and Mackay, D. (1996) Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology* 30, 390A–396A.
- Wong, G. T. F. (1995) Dissolved iodine across the Gulf Stream Front and in the South Atlantic Bight. *Deep-Sea Research I* **42**, 2005–2023.
- Zhou, J. N. L., Fileman, T. W., Evans, S., Donkin, P., Mantouri, R. F. C. and Rowland, S. J. (1996) Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary and Humber coastal zone. *Marine Pollution Bulletin* 32, 599–608.